



(11) (A) No. 1 162 511

(45) ISSUED 840221

(52) CLASS 204-91.27

³
(51) INT. CL. B01J 19/10,
C07C 19/08

(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR THE PREPARATION OF 2-CHLORO-1,1,1,2,3,3,3-
HEPTAFLUOROPROPANE

(72) von Halasz, Sigmar-Peter,
Germany (Federal Republic of)

(73) Granted to Hoechst Aktiengesellschaft
Germany (Federal Republic of)

(21) APPLICATION No. 376,831

(22) FILED 810504

(30) PRIORITY DATE Germany (Federal Republic of)
(P 30 17 154.1) 800505

No. OF CLAIMS 3 - NO DRAWING

Canada

Abstract:

Process for the preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane

The invention relates to a process for the selective preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane, wherein 1,1,1,2,3,3,3-heptafluoropropane is reacted in the gas phase with elementary chlorine in the presence of high-energy radiation at reaction temperatures in the range of from -30° to $+500^{\circ}\text{C}$.

The present invention relates to a process for the selective preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoro-propane ("2-chloro-heptafluoropropane") by photochlorination of 1,1,1,2,3,3,3-heptafluoropropane ("2H-heptafluoropropane").

2-Chloro-heptafluoropropane (boiling point -2°C) belongs to the category of the completely halogenated alkanes, which is distinguished by exceptional thermal and chemical stability, non-flammability and special electrical and other physical properties. 2-Chloro-heptafluoropropane can be employed, inter alia, as a coolant or heat transfer medium, as an inert solvent or cleaning agent for low temperature use, as a gaseous or liquid inert medium, for example as a dielectric or insulating medium, as a fire-extinguishing agent or additive to fire-extinguishing agents, or as an etchant for silicon dioxide layers on silicon. In the patent literature, 2-chloro-heptafluoropropane has been proposed as a blowing agent or blowing agent component (U.S. Patent 4,057,973), and for the preparation of soluble, fusible polymers of low flammability from more easily flammable polymers by irradiation (German Patent 1,213,117). Accordingly, there is considerable interest in a simple and economical process, which does not pollute the environment, for the preparation of the compound shown in the title.

2-Chloro-heptafluoropropane has already been described repeatedly in the literature. Most processes for its preparation are based on the fluorination



of a C_3 -compound:

Thus, according to U.S. Patent 2,466,189, the compound $CF_3CClFCF_3$ can be obtained by fluorinating 2-chloropentafluoropropene with hydrogen fluoride and lead
5 dioxide in an autoclave, whilst according to British Patent 839,034 it can be obtained by an addition reaction of elementary fluorine with 2-chloropentafluoropropene. The fluorination of 1,1,1-trifluoro-tri-
chloropropene by means of cobalt trifluoride, in accordance with U.S. Patent 2,670,387 also produces 2-chloro-
10 heptafluoropropane, in low yield.

The fluorination of 3-chloro-prop-2-ene with hydrogen fluoride at temperatures above $500^{\circ}C$, in
accordance with the process of U.S. Patent 3,047,641,
15 results in a yield of about 50% of the title compound. According to U.S. Patent 2,831,035, the reaction of fluorine or of chlorine trifluoride with $CF_3CCl_2CClF_2$
or $CF_3CCl_2CCl_2F$ in the presence of an aluminum fluoride catalyst results in the formation of not only octa-
20 fluoropropane but also 2-chloro-heptafluoropropane.

On a laboratory scale, the title compound can be prepared in yields of over 80% by an addition reaction of chlorine fluoride with hexafluoropropene (D. D. Moldavski, V. G. Temchenko et al., Zh. Org. Khim. 9,
25 673). However, transfer of this process to an industrial scale is difficult, since by-products which are difficult to separate off are formed and the chlorine fluoride employed is highly toxic, is awkward to handle, since, for example, it reacts vigorously with glass and

explosively with hydrogen-containing compounds, and must, furthermore, in its turn be prepared from elementary fluorine and chlorine.

None of the known processes is suitable for the selective preparation of 2-chloro-heptafluoropropane in high yields. In all the processes, fragmentation reactions or other competitive reactions occur to a considerable degree. The undesired by-products reduce the yield and make extensive distillation operations necessary. Furthermore, the known methods of preparation require starting compounds which are difficult to obtain, uneconomical fluorinating agents or high reaction temperatures, which result in increased corrosion of the reactor materials and short lives of catalysts.

Accordingly, there existed the problem of providing a simple process for the selective preparation of 2-chloro-heptafluoropropane, which is based on easily accessible starting materials and proceeds with high yields.

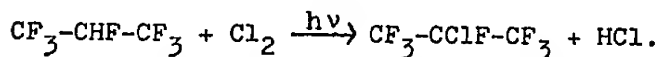
This problem is solved by the invention defined in the main claim.

The process according to the invention can be operated continuously in the manner of conventional gas/gas reactions. A solid catalyst is not required for this purpose. The preferred temperature range is from 20 to 450°C, especially from 30 to 400°C, and more particularly from 40 to 350°C.

High-energy light means, in the present context,

radiation which is capable of decomposing chlorine molecules into chlorine atoms, in particular visible light and ultraviolet light in the range of from 450 to 260 nm. The process according to the invention

5 can be described by the equation



The reaction can be carried out in a conventional irradiation apparatus, such as is used, for example, for chlorinating toluene to give benzyl
10 chloride. Such an apparatus consists, for example, of a glass flask into which a mercury high-pressure immersion lamp provided with a quartz tube is introduced. The glass flask is additionally equipped with a gas inlet tube, an internal thermometer, a condenser
15 which is cooled with carbon dioxide, and a drainage stopcock attached to the bottom. The glass flask should be capable of being externally heated at the level of the immersion lamp and at the level of the drainage stopcock.

20 In general, the metered gaseous starting products are introduced as a mixture into the glass flask. The gas mixture leaving the reactor is washed with water, whereby hydrogen chloride formed is absorbed. Thereafter, the residual chlorine is removed with thio-
25 sulfate solution and dilute sodium hydroxide solution and the product is dried by means of towers which are filled with calcium chloride or with phosphorus pentoxide. The crude product can be condensed in suitable cold traps.

The boiling points of starting materials and end products are summarized in the table below:

Product or material	Formula	Molecular weight	Boiling point/ 1 bar
2H-Heptafluoropropane	$\text{CF}_3\text{CHF}\text{CF}_3$	170.03	-18°C
5 Chlorine	Cl_2	70.96	-34.1°
Hydrogen chloride	HCl	36.46	-85°
2Cl-Heptafluoropropane	$\text{CF}_3\text{CCl}\text{FCF}_3$	204.47	-2°

The 2H-heptafluoropropane employed is of technical-grade purity and is advantageously anhydrous, ie. it is preferably dried with phosphorus pentoxide. 2H-Heptafluoropropane is easily obtainable by the quantitative addition reaction of hydrogen fluoride with hexafluoropropene, for example in accordance with German Offenlegungsschrift 2,712,732. Chlorine is taken from a commercial steel cylinder and is advantageously employed in the anhydrous form, ie. it is dried with, for example, concentrated sulfuric acid.

The conversion of 2H-heptafluoropropane at 300° and atmospheric pressure is about 0.1 to 3 moles/l of reactor volume per hour, depending on the radiation intensity. Lower throughputs are readily achievable. At higher pressures, the conversion can be correspondingly higher. In general, the chlorine is added without dilution; the amount of chlorine is in general between 0.1 and 3.5 moles/l of reactor volume per hour. The amount of chlorine should be at least equivalent to the amount of 2H-heptafluoropropane, which is added simultaneously

and continuously. A slight excess of chlorine is preferred. The molar ratio of 2H-heptafluoropropane/chlorine is, for example, between 1 : 1.5 and 1 : 1, preferably between 1 : 1.15 and 1 : 1.05. Quantitative conversion of 2H-heptafluoropropane can be achieved by using an excess of chlorine. Whilst larger excesses of chlorine are feasible, they are not advantageous, since, if an efficient condenser is used, there is the danger that unconverted chlorine liquefied in the condenser and flowing back into the irradiation reactor may lower the temperature in the reactor and accordingly lead to a reduction in the rate of reaction. Furthermore, the excess of chlorine increases the effort entailed in working up by distillation. Any major excess of chlorine is advantageously removed from the gaseous reaction products by fractional distillation; the recovered chlorine can be re-used. Whilst it is possible to employ a less than equivalent amount of chlorine, this reduces the conversion and increases the effort entailed in working up.

In general, the process is carried out without addition of an inert gas. Whilst dilution with an inert gas, such as, for example, nitrogen, is feasible, it does not offer any significant advantages.

The irradiation reaction can be carried out over a wide temperature range, of from -30° to $+500^{\circ}\text{C}$; however, the reaction proceeds only slowly in the range of from -30° to $+40^{\circ}\text{C}$. Accordingly, temperatures above 40°C are preferred. Whilst temperatures in the

range of from 350 to 500°C are feasible they are disadvantageous from the point of view of energy consumption.

5 The residence time of the starting materials
and of the end products in the reactor is not critical;
it can, for example, vary between a few seconds and a
few minutes, without the composition of the crude products being adversely affected by the occurrence of
side-reactions or secondary reactions. On the other
10 hand, economical considerations impose an upper limit
on the residence time. Accordingly, it is advantageous, for a high space-time yield, that the reaction
products formed should be removed from the reactor as
promptly as possible.

15 The hydrogen chloride formed is in general discharged at the top, through a condenser cooled with
solid carbon dioxide. The 2-chloro-heptafluoropropane formed, which collects at the bottom of the
reactor, can also be taken off continuously, through a
20 stopcock.

 The process according to the invention is in
general carried out under atmospheric pressure, but the
use of reduced pressure or superatmospheric pressure
(for example up to 10 bar, preferably up to 3 bar) is
25 also possible, within wide limits. In order to
achieve high space-time yields, it is preferred to use
superatmospheric pressure.

 For reactions on an industrial scale, a continuous and uniform method of operation is desirable. In

the process according to the invention, continuous introduction of chlorine and 2H-heptafluoropropane, continuous conduct of the reaction, continuous discharge of the reaction products and continuous working up are readily possible. Further particular advantages of the continuous procedure are the improved utilization of the starting materials and the small amount of effluent and waste gas produced.

In the process according to the invention, the conversion of 2H-heptafluoropropane is in general above 90% and often above 99%.

Because of the high selectivity of the process according to the invention, the yields of 2-chloro-heptafluoropropane are also above 90% and often above 98% of theory. The 2-chloro-heptafluoropropane produced is obtained in high purity. Working up is therefore extremely simple.

In view of literature statements concerning the lack of reactivity towards chlorine of hydrogen atoms in the immediate vicinity of trifluoromethyl groups, it is surprising that the substitution of hydrogen by chlorine in 2H-hexafluoropropane proceeds so smoothly in the process according to the invention.

It is known that in comparable compounds such as $\text{CF}_3\text{-CH}_2\text{-CF}_3$ and $\text{CF}_3\text{-CH}(\text{CCl}_3)\text{-CF}_3$, hydrogen is not replaced by chlorine (Houben-Weyl, Methoden der organischen Chemie (Methods of Organic Chemistry), 1962, volume V/3, pages 594-598).

The process is illustrated by the Examples which follow.

Example 1

The experimental arrangement consists of a multi-neck irradiation flask made of [®] DURAN glass, which has a capacity of 2 liters and into which an ultraviolet high-pressure mercury immersion lamp provided with a thin-walled quartz glass tube is introduced. The irradiation flask is additionally equipped with a gas inlet tube, which terminates near the immersion lamp, an internal thermometer, which extends into the vicinity of the immersion lamp, a condenser filled with solid CO₂, which is placed on one of the ground-glass connections attached to the top, and a drainage stopcock located at the bottom of the irradiation flask. The outer walls can be additionally heated externally, by means of electrical radiant heaters, at the level of the immersion lamp and at the level of the drainage stopcock. Both the upper exit of the condenser and the exit of the drainage cock lead to a wash vessel, filled with water, to take up the hydrogen chloride formed. These wash vessels are followed by wash vessels filled with aqueous 10% strength Na₂S₂O₃ solution to take up the excess chlorine, and vessels filled with aqueous 10% strength NaOH for the final wash. These are then followed by two drying towers, one filled with CaCl₂ for pre-drying and the other filled with P₂O₅ for final drying. The gaseous crude product is finally condensed in a high-efficiency cold

trap, cooled with CO_2 .

Elementary chlorine is taken from a commercial steel cylinder, dried with concentrated H_2SO_4 , metered by means of a flowmeter and mixed with the stream of

5 CF_3CHF_3 gas.

2H-Heptafluoropropane is prepared in accordance with German Offenlegungsschrift 2,712,732, by hydrofluorination of hexafluoropropene in the presence of a chromium oxyfluoride catalyst. It is dried with

10 P_2O_5 , metered by means of a flowmeter and mixed with the stream of Cl_2 .

Before starting the photochlorination, the reaction chamber, which has beforehand been flushed with N_2 , is pre-heated by switching on the ultraviolet lamp;

15 this results in temperatures of about 150° to 180°C in the reactor chamber. In the immediate vicinity of the immersion lamp, temperatures of 260° to 300°C are measured on the quartz glass.

To photochlorinate 2H-heptafluoropropane, a total

20 of 76 g (0.45 mole) of CF_3CHF_3 and 33 g (0.46 mole) of chlorine, corresponding to a molar ratio of $\text{CF}_3\text{CHF}_3 : \text{Cl}_2$ of 1 : 1.02, is introduced in the course of 2 hours, at temperatures of 120° to 90°C . During the experiment, the hydrogen chloride evolved which is

25 not retained by the condenser is absorbed in the wash water receiver. After completion of the reaction, flushing with N_2 is employed in order to wash the entire hydrogen chloride into the wash water. In the present example (1) the other gaseous reaction products,

which collect at the bottom of the irradiation vessel, are discharged through the drainage stopcock, located at the bottom, only after completion of the reaction.

0.44 mole of HCl is found, by titration, in the wash water; HF is not found. The condensed crude product is examined by gas chromatography on a [®] PORAPAK column. This reveals the following:

	$\text{CF}_3\text{CClFCF}_3$	98.1%
	CF_3CHF_3	1.7%
10	$\text{CF}_3\text{CClFCClF}_2$	0.1%
	CF_3CF_3	< 0.05%
	$\text{CF}_3\text{CF}_2\text{CF}_3$	< 0.05%

The two last-mentioned components are unconverted impurities of the heptafluoropropane employed;

15 $\text{CF}_3\text{CClFCClF}_2$ is produced by chlorination of C_3F_6 , which is also present in traces in the starting material.

The liquid crude product weighs 88 g. Accordingly the yield of $\text{CF}_3\text{CClFCF}_3$ is 95.4% of theory, based on CF_3CHF_3 converted. The 2-chloro-1,1,1,2,3,3,3-hepta-
20 fluoropropane is additionally identified by ¹⁹F-NMR measurement, infrared recordings and determination of the boiling point, which is -2°C.

Example 2

CF_3CHF_3 is photochlorinated, at temperatures
25 of 115° to 110°C at the beginning of the experiment and temperatures of 35° to 20°C at the end of the experiment, by passing into the apparatus of Example (1), in the course of 5.5 hours, a total of 467 g (2.75 moles) of CF_3CHF_3 and 198 g (2.79 moles) of Cl_2 , corresponding

to a molar ratio of CF_3CHF_3 : Cl_2 of 1 : 1.01. The condensed reaction products which collect at the bottom of the irradiation flask are, as in Example (1), removed via the drainage stopcock only after completion of the experiment, and are then washed.

1.84 moles of HCl are found by titration in the wash water of the gases. Analysis by gas chromatography reveals the following composition of the condensed crude product:

10	$\text{CF}_3\text{CClFCF}_3$	67.5%
	CF_3CHF_3	32.1%
	3 other components each	0.1%

The condensate weighs 512 g. The yield of $\text{CF}_3\text{CClFCF}_3$ is accordingly 90.5% of theory, based on CF_3CHF_3 converted; however, the conversion of CF_3CHF_3 is only about 68%.

Example 3

A total of 495 g (2.91 moles) of CF_3CHF_3 and 217 g (3.06 moles) of chlorine, corresponding to a molar ratio of CF_3CHF_3 : Cl_2 of 1 : 1.05, are introduced as gas, in the course of 5 hours, into the apparatus of Example (1), at temperatures of 120° to 110°C , which can be maintained over the entire experiment. The reaction products which collect are discharged continuously and uniformly via the drainage stopcock, located at the bottom of the irradiation flask, except for a constantly remaining residual amount of about 10 to 15 ml, and are then washed.

2.76 moles of HCl are found in the wash water of

the gases. Gas chromatography measurements on the collected condensed crude product show the following composition:

5	$\text{CF}_3\text{CClFCF}_3$	95.3%
	CF_3CHF_3	3.9%
	Remainder: secondary components	0.8%.

The condensate weighs 585 g. Accordingly the yield of $\text{CF}_3\text{CClFCF}_3$ is 97.6% of theory, based on CF_3CHF_3 converted.

10 Example 4

A total of 1,080 g (6.35 moles) of CF_3CHF_3 and 526 g (7.41 moles) of chlorine, corresponding to a molar ratio of $\text{CF}_3\text{CHF}_3 : \text{Cl}_2$ of 1 : 1.17, is introduced, in the course of 7.5 hours, into the apparatus of Example (1), at temperatures of 135° to 125°C . The outer walls of the flask are additionally heated, at the level of the immersion lamp and of the drainage stop-cock, by means of electrical radiant heaters. As in Example (3), the reaction products which collect are discharged continuously and uniformly from the flask.

6.31 moles of HCl are found in the wash water. Analysis by gas chromatography reveals the following composition of the crude product:

25	$\text{CF}_3\text{CClFCF}_3$	99.7%
	CF_3CHF_3	0.15%
	$\text{CF}_3\text{CClFCClF}_2$	< 0.02%
	$\text{CF}_3\text{CF}_2\text{CF}_3$	< 0.05%
	$\text{CF}_3\text{CHFCClF}_2$	0.1%

- 15 -

The condensate weighs 1,289 g; accordingly the yield of $\text{CF}_3\text{CClFCF}_3$ is 99.1% of theory, based on CF_3CHF_3 converted. The conversion of CF_3CHF_3 is 99.85% of theory.

PATENT CLAIMS

1. A process for the selective preparation of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (I), wherein 1,1,1,2,3,3,3-heptafluoropropane (II) is reacted in the gas phase with elementary chlorine in the presence of high-energy radiation at reaction temperatures in the range of from -30° to $+500^{\circ}\text{C}$.
2. A process as claimed in claim 1, wherein (II) is reacted with chlorine in a molar ratio of 1 : 1.0 to 1 : 1.5, preferably of 1 : 1.05 to 1 : 1.15.
3. A process as claimed in claim 2, wherein the reaction temperatures are from 40° to 450°C .

Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents

